

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improvements in or relating to Fluorocarbon Polymeric Matrices

5 We LEESONA CORPORATION, a corporation organized and existing under the laws of the Commonwealth of Massachusetts, United States of America of 333, Strawberry Field Road, Warwick, State of Rhode Island, United States of America. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to the production of a porous hydrophobic matrix, having pre-determined wetting characteristics, useful as filters, separators, diaphragms and the like. More particularly, the invention relates to porous membranes or shaped articles of sinterable, corrosion and heat resistant fluoro-polymers. The invention will be described hereinafter with particular reference being made to elements such as porous barriers, supports in electrode construction, or matrices for retaining an electrolyte, for use in an electrochemical cell, and more particularly in a fuel cell. It is to be understood, however, that the materials of the invention have other utility where the peculiar characteristics of the composition are important as will be apparent to one skilled in the art. Reference to a fuel cell is by way of convenience and sets forth a preferred utility for the materials.

15 The principal requisites of a matrix or separator of the class useful in electrochemical cells are maximum chemical stability, low electrical resistance, and maximum diffusion of electrolyte in order to minimize the internal resistance of the over-all assembly. Other necessary properties include sufficient mechanical strength to withstand handling during assembly of the cell, shape and dimensional stability when wet with electrolyte, con-

45 trolled porosity and sufficient density to act as a physical barrier to resist penetration of the matrix by the gaseous reactants piercing the separator and possible short circuiting of the cell by metallic growths.

50 For optimum performance in a fuel cell employing a trapped aqueous electrolyte, the matrix should be wettable by the electrolyte to the extent that the electrolyte forms a continuous phase which is in intimate contact with one surface of each electrode. Moreover, the combination of matrix and electrolyte must act as an effective bubble barrier to avoid the mixing of reactant gases at one electrode surface and thus to prevent reactions of an explosive nature. The electrolyte matrix must also have a porosity sufficient to permit the necessary ionic mobility requisite to the ionic conductance internal to the cell structure at minimum resistivity and be inert to the electrolyte impregnated therein. To avoid a current flow within the electrolyte systems per se, with consequent wastage of utilizable power, the matrix must be an excellent electrical insulator. The matrix must also have a sufficient degree of pliability to conform to the surfaces of the electrodes of the cell so as to maintain the highest degree of area of contact therebetween and avoid areas of separation therefrom. Since the matrix must also function as a physical barrier to the mixing of the gaseous reactants, the matrix for a trapped electrolyte is ordinarily employed in fuel cell constructions wherein the matrix is compressed about the peripheral edges in sealing engagement with a suitable apertured framing members and/or cooperable sealing means or gasket. Therefore, the matrix preferably will have properties commendable to gasketing or sealing means. To minimize the cost the matrix should be constructed of materials which are

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readily available and manufactured by a quick, easy, efficient process, and the matrix preferably should be re-utilizable by replenishing with fresh aqueous electrolyte.

5 Materials currently employed as matrices for trapped electrolyte systems include various materials such as modified cellulose and pressed mineral fibers such as asbestos, alumina, and magnesia. Such materials cur-  
10 rently in use as matrix-forming materials suffer from a number of serious drawbacks, the principal among them being lack of chemical and/or thermal stability and poor mechanical strength. By way of example, asbestos im-  
15 pregnated with an aqueous alkali such as potassium hydroxide is readily attacked to produce gelatinous residues which interfere with the ionic conductance, increase internal cell resistance and are incapable of being  
20 reimpregnated with fresh electrolyte. Modified cellulose, on the other hand, is easily hydrolyzed by the electrolyte.

The use of microporous polymeric films as elements in electrochemical cells, such as  
25 battery separators, is not new. For example, United States Patents Nos. 2,542,527 and 2,676,929 disclose processes wherein poly-  
30 meric materials such as polyvinyl chloride or polyethylene are admixed with finely-ground starch particles and the mixture cast into sheets. The starch particles are  
35 hydrolyzed and rendered soluble by successive treatments and washing in both acid and alkaline media, leaving in their place  
40 voids of the approximate size of the original particles. While this type of microporous material has found some commercial applica-  
45 tion in the battery art, its principal disadvantages are the relatively high cost of manufacture, the difficulty experienced during  
50 manufacture in maintaining control of the pore size in the finished product, mechanical weakness of the resultant matrix, and the  
55 inability of the process to achieve pores with surfaces of controlled wetting characteristics, which are desirable in many fuel cell  
60 applications.

Accordingly it is one object of the present invention to provide a method for fabricat-  
50 ing a matrix free, or substantially free, of the defects associated with the aforementioned matrices of the prior art.

According to the invention there is provided a method for preparing porous shaped  
55 bodies comprising a hydrophobic polymeric matrix having preselected wettable characteristics, which method comprises the steps of precipitating a fluorocarbon polymer onto  
60 loose fibers having a charge opposite to that of said polymer to form a polymer-fiber aggregate, forming said aggregate into a desired shape, elevating said formed aggregate to a temperature at which said precipitated poly-  
65 mer will sinter, maintaining said aggregate at said temperature for a time sufficient to

cause said polymer to sinter and form a pliable and coherent mass and consume said  
fibres, thus exposing the volume previously occupied by said consumable fibers to  
70 ambient atmosphere.

The invention also provides a hydrophobic polymeric matrix having preselected wettable characteristics comprising a continuous phase  
75 of sintered fluorocarbon polymeric material having a series of integral interconnecting pores and a discontinuous colloidal mineral phase deposited in said pores, said mineral phase being uniformly arranged from major surface to major surface of said matrix.

The porous fluoropolymer matrix may be made by precipitating the polymer from a  
80 colloidal state onto a loose slurry of selected and oppositely charged fibers, such as cellulose fibers. The charge on the fibers is induced by the adsorption of cationic agents  
85 on their surface. The fiber/polymer ratio and the diameter of the fiber determine porosity and pore size, respectively. The plastic coated coagulum is extracted from the slurry and  
90 dried. The fibers may be either re-slurried in water and re-deposited upon a paper mat by processes known to the art or compressed into a sheet in a suitable mold. The dried  
95 sheet or mat is placed in a furnace adjusted to the sintering temperature of the hydrophobic polymer, causing the fibers to burn out, leaving a porous plastic structure behind.

Varying wetting characteristics and pore surface texture can be produced by adsorb-  
100 ing a colloidal mineral of desired dimensions onto the surface of the fiber in an aqueous medium and precipitating the finely divided particulate fluoro-polymer from an aqueous  
105 dispersion onto the mineral modified surface of the fiber, and collecting the resulting coagulum. The coagulum can be formed into any desired shape, which is then subjected to elevated temperatures sufficient to cause  
110 the particulate hydrophobic polymer to sinter to a pliable coherent mass and to cause the fibrous substrate to undergo combustion thus exposing the volume previously occupied by  
115 the fibrous substrate to the ambient atmosphere, and leaving the colloidal mineral distributed uniformly throughout the pore structure and firmly held therein. In an electrolyte matrix the mineral additives, or fillers, act  
120 as "stepping stones", allowing the "electrolyte" to achieve ionic conductive continuity between the electrodes as a result of their particular wetting characteristics. Any carbonaceous residue in the structure can be removed by treating the sintered material  
125 with a strong oxidizing acid, such as nitric acid, prior to the final drying. The resulting composition has a pore surface texture and chemical composition which is readily wettable by an aqueous electrolyte. The elec-  
130 trical resistivity of the porous material when

used as a matrix for a trapped electrolyte, or as a support for an electrode, is materially reduced and the ionic conductivity enhanced to a high degree.

5 In practicing the present invention, a staple cellulosic or similar fiber of the desired dimensions can be suspended in an aqueous medium by such conventional methods as the action caused by a plurality of blades rotating at high speeds to produce a severing action upon the fibrous material, and thereby causing the formation of a pulp or suspension of fibers corresponding to the desired dimensions of the ultimate pore structure of the matrix. A colloidal mineral can be added to the resulting suspension and caused to sorb upon the surface thereof by the addition of cationic agents or like means. The particulate hydrophobic polymer is precipitated from a colloidal state into a loose slurry of the fibers, or the polymer is added to the aqueous dispersion of fibers, and a coagulating or flocculating agent added to cause coagulation or precipitation to form a polymer/fiber coagulum, or a polymer/colloidal mineral/fiber coagulum or aggregate. The coagulum is capable of separation and extrusion by conventional processes to form articles of any desired shape suitable for the ultimate purposes intended. The shaped article is subjected to temperatures sufficient to cause sintering of the particulate polymer, causing formation of a coherent pliable mass having a porosity controlled by the amount of cellulosic fibers therein, through combustion of the fibers forming a carbonaceous combustion product and thereby exposing the volume previously occupied by the cellulosic fiber.

40 The preliminary coalescence of the polymer/fiber, or polymer/colloidal mineral/fiber aggregate to form the sinterable stock of the present invention is accomplished by an organic coalescing or flocculating agent which is mixable with water and in which the polymeric material is substantially insoluble. Exemplary flocculating or coalescing agents include acetone, methyl ethyl ketone, methanol and ethanol. The sinterable stock from the initial coalescing can be formed into membranes or other desired shapes through conventional extrusion or orifices, extrusion slots or by resuspension in an aqueous medium and collection by mechanical means, such as forced filtration of the aqueous phase.

55 Complete coalescence of the polymer particles to form a continuous polymeric phase in the formation of the porous article is achieved by sintering. Development of optimum mechanical properties is dependent in part upon the ratios of polymer:mineral: fibrous substrate as well as in part upon the sintering conditions, since incomplete sintering results in weak spots and corresponding poor mechanical properties. The optimum

sintering temperature appears to be approximately 350—400°C. although temperatures as high as 430°C. can be successfully employed with some fluoro-polymers such as polytetrafluoroethylene. In general, sintering is effected at a temperature between the crystalline melt point, e.g., in the case of polytetrafluoroethylene, 327°C., and the decomposition temperature of the hydrophobic polymer. While higher temperatures in general require shorter sintering times, temperatures in excess of 400°C., e.g. in the case of polytetrafluoroethylene, tend to promote appreciable degradation. Any suitable heating media such as the hot air of a muffled furnace, radiant heat, and heated rollers or platens may be employed in the sintering operation.

Although particular reference has been made hereinbefore to polytetrafluoroethylene, which is the preferred polymer in the practice of the present invention, other polyhalogenated polymers can be used. By way of example copolymers of tetrafluoroethylene with other unsaturated organic compounds such as perfluoropropylene and chlorotrifluoroethylene may be employed provided such copolymers maintain the essential properties of the tetrafluoroethylene homopolymer. In general, copolymerizable modifiers may be present in an amount up to about 15% by weight of the copolymer without destroying or deviating from the advantageous properties of the tetrafluoroethylene. Other polymeric materials usable herein are polymers of fluorinated propylene, vinylfluoride, vinylidene fluoride, and copolymers thereof.

The production of the fluoro-polymer dispersion is not a part of the present invention. The dispersion may be prepared by any suitable process described in the existing art including, by way of example, procedures disclosed in U.S. Patent No. 2,478,229; U.S. Patent No. 2,534,058; U.S. Patent No. 2,559,750; and U.S. Patent No. 2,685,707. The particle size of the polymer in the dispersions employable in the practice of the present invention may vary over a wide range. Preferably, the particles of the polymer should be of a colloidal state, e.g., a practical size range being from 0.05 to 5 microns and, more preferably, from 0.1 to 3 microns in size. The smaller the particles the more easily is the formation of the sinterable stock and the workup of the sinterable stock to the ultimate, porous shaped structure. The fluoro-polymer can vary widely as to molecular weight. Advantageously, molecular weights for the fluoro polymer of 8,000 or higher are employed. As employed herein the term "hydrophobic polymer" or "fluoro-polymer" refers to polymers such as, e.g., polytetrafluoroethylene, noted above, which have crystalline melt temperatures above about 300°C. and are sinterable at temperatures from

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around their crystalline melt temperature to the decomposition temperature of the respective polymer. Suitable starting materials of this type include aqueous suspensions containing 60% by weight of polytetrafluoroethylene particles, for example those available under the trade names "Teflon" 30 and "Teflon" 41X ("Teflon" is a Registered Trade Mark). Such dispersions may contain compatible wetting agents which may be of cationic, non-ionic and anionic types. Where the polymeric dispersion contains such wetting or stabilizing agents, precipitation of the particulate polymer onto the surfaces of the cellulosic fibrous substrate or cellulosic fibrous substrate modified with colloidal mineral is facilitated by use of precipitating agents inducing the opposite charge upon the substrate particles.

The fibrous pore-forming substrate can be formed by any conventional mechanical and/or chemical pulp-forming procedure employed in the paper-making or like art. The fibrous pulp can be prepared from flax, cereal straws, wood products and like cellulosic pulp rendering starting materials. The degradation by mechanical and/or chemical means is continued until a fibrous pulp suspension is obtained having the requisite dimensional parameters. As the size of the pore structure in the ultimate sintered composition corresponds closely to the dimension of the volume occupied by the fibrous substrate prior to combustion thereof to form the gaseous product which exposes the volume to ambient atmosphere, the dimension of the fibrous substrate employed in compounding the sinterable stock will depend upon the use and characteristics desired of the ultimate porous membrane composition. By way of example, in the use of the sinterable stock to form a porous wettable membrane matrix for trapped electrolytes in gas-consuming fuel cells, a fibrous suspension wherein the individual fibers have an average cross section of from 0.5 to 20 microns and more advantageously from 1 to 5 microns is preferred. For other uses such as battery diaphragms and electrode supports, the fibers can have an average diameter of from 0.5 to 200 microns. The length of the fiber can vary, again being determined by its ultimate use. In general fibers having an average length of from 5 microns to 10 millimeters can be employed.

In a preferred embodiment of the invention, colloidal mineral components or other non-consumable and hydrophilic materials increasing the wettability of the hydrophilic fluoro-plastics are incorporated into the pore structure of the matrix by sorbing suitable colloidal minerals on fibrous cellulose prior to the deposition of the colloidal hydrophobic polymer to form the coagulum or aggregate. When the final structure is subjected to the sintering temperatures of the

fluoro-polymer the cellulosic material burns out leaving the wetting filler deposited in the pore structure previously occupied by the cellulosic material and now exposed to ambient atmosphere by the decomposition gases. The resulting structure is characterized by good mechanical strength, high porosity, selective wetting characteristics and excellent stability to chemical attack by the electrolytes. The electrolyte-stable aqueous wettable fillers function as "stepping stones" to permit the electrolyte to achieve a phase continuity over the surfaces defining the pores of the porous matrix between the electrodes. For optimum capillary requirements the electrolyte-stable wettable fillers should preferably have a particle size in the 0.01 to 0.2 micron range and be present in relation to the fluorocarbon polymer at a ratio of from 0.1 to 10.0 on a weight basis. Matrices particularly suitable will employ a particulate fluorocarbon polymer having an average particle size of from 0.1 to 50 microns, with the pores having an average diameter of from 0.5 to 10 microns and the colloidal mineral filler having an average particle size of from 0.01 to 0.2 microns. To have the most efficient electrolyte wetting, the mineral phase should be uniformly arranged from major surface to major surface of the matrix. Exemplary wettable fillers for filling the aforesaid capillary requirements include exploded silicon dioxide, potassium titanate, titanium dioxide, thoria and zirconia. Exploded silicon dioxide is a material obtained by heating silica containing some free water or water of hydration which causes the silica to be blown up as a very porous material. This material is crushed to provide silica particles which are very finely divided but still porous. The aforesaid wettable fillers may be in fibrous or powder form.

Having described the invention in general terms, to more particularly illustrate the invention a detailed working example will be set forth.

#### EXAMPLE

Twelve grams of ashless filter paper (no. 41 Watman), 250cc's of distilled water, and one cc of a 10% aqueous solution of trimethyl pelargonate ammonium hydrochloride, and 6 grams of colloidal silica, are charged to a Waring type blender and mixed for fifteen minutes at approximately three-quarters the rated capacity of the blender. Sixty grams of a 50% by volume aqueous dispersion of polytetrafluoroethylene, stabilized with a non-ionic surfactant, is added to 100cc's of distilled water and the mixture charged to the blender while the blender is turned on at 30% of the maximum speed. After all the dispersion has been added the resultant charge is agitated for an additional fifteen minutes. Thereafter, with the mixture subjected to a constant

speed, approximately 30% of the maximum blender speed, 150cc's of acetone are added and the mixture stirred for an additional five minutes.

- 5 The coagulated slurry is collected by filtration in a vacuum funnel and the resultant cake dried at 100°C. at 25 inches (Hg) of vacuum for sixteen hours. The resulting dried cake is broken up in the blender until a
- 10 loose, fluffy, fibrous product is obtained. Three grams of the resultant loose fibers and 150cc's of distilled water are mixed in the blender at high speed for one minute. Trapped air is removed in a vacuum assembly. A 9
- 15 centimeter filter paper is placed on a vacuum funnel and the slurry deposited thereon. The slurry is allowed to settle slowly in the absence of a vacuum for approximately two minutes and a vacuum then applied until
- 20 water is no longer extractable. The upper surface can be rendered more even by pressing down upon the mat with a filter paper of the same size as below. The resulting slurried cake is dried overnight at 150°F.
- 25 The filter papers are removed and the mat placed in a muffle furnace at 670°F. for 15 minutes, or until all the cellulose is burned out. The mat is allowed to cool slowly at room temperature and the resultant porous plastic sheet is placed in a hot nitric acid reflux assembly and boiled until the poly-
- 30 meric material achieves its characteristic off-white color. The matrix as prepared above has excellent utility in a fuel cell for retaining an aqueous electrolyte, or as a support in electrode construction. In the electrode construction, one surface of a thin sheet of the matrix is coated with an activating material such as platinum black and the
- 35 polytetrafluoroethylene surface maintained in contact with fuel gas, with the activated surface being in contact with the electrolyte.
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- 45 Additionally, in the Example, prior to the addition of the polymer dispersion, chemically stable wettable fillers such as exploded silicon dioxide, potassium titanate, titanium dioxide, thorium or zirconia, either in powder or fiber form, can be added to the fibrous suspension. The resultant product will be
- 50 similar to the product obtained in the example except that the inert filler will be present at the porous openings of the plastic matrix. This expediency permits the tailormaking of the matrix as to surface properties, such as wetting and the like.
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- 60 Although the present invention has been described with emphasis being placed upon fuel cell applications, it is apparent, as noted in the preamble of the specification, that the described structures will have numerous applications as filters, diaphragms and the like. The hydrophobic polymer structures can be made having varying porosities and pore sizes, including membranes where the actual
- 65 porosity is not discernible, i.e., where it is

doubtful whether the pores are in the sub-micron range or are present as simple spaces between molecular chains. Since the pore size can be accurately determined, and because of the chemical inertness and heat resistant properties of the matrices, they can be used in numerous applications which will be apparent to one skilled in the art. Furthermore, according to the present invention it is possible to construct the novel matrix around a support such as a metal screen to improve its mechanical stability and render the matrix electrically conductive. The various modifications of the matrices and their numerous applications are to be included herein, with the invention only being limited by the appended claims.

#### WHAT WE CLAIM IS:—

1. A method for preparing porous shaped bodies comprising a hydrophobic polymeric matrix having preselected wettable characteristics, which method comprises the steps of precipitating a fluorocarbon polymer onto loose fibers having a charge opposite to that of said polymer to form a polymer-fiber aggregate, forming said aggregate into a desired shape, elevating said formed aggregate to a temperature at which said precipitated polymer will sinter, maintaining said aggregate at said temperature for a time sufficient to cause said polymer to sinter and form a pliable and coherent mass and consume said fibers, thus exposing the volume previously occupied by said consumable fibers to ambient atmosphere.
2. A method as claimed in claim 1, wherein said consumable fibers are a cellulosic material oxidizable to a carbon-containing gas at the sintering temperature of the fluorocarbon polymer.
3. A method as claimed in claim 1 or claim 2, wherein the fluorocarbon polymer is polytetrafluoroethylene.
4. A method as claimed in any of the preceding claims, wherein an aqueous, wettable, finely divided particulate mineral is adsorbed on the fibers before said fluorocarbon polymer is precipitated.
5. A method as claimed in claim 4, wherein said wettable mineral has a particle size from 0.01 to 0.2 microns.
6. A method as claimed in any of the preceding claims, comprising absorbing a cationic agent onto the surface of the cellulosic fibers before the hydrophobic polymer is precipitated.
7. A method as claimed in any of the preceding claims, wherein the cellulosic fibers have an average cross section of 0.5 to 20 microns and an average length from 5 microns to 10 millimeters.
8. A method as claimed in any of the preceding claims, wherein the ratio of polymer

to cellulosic fibers is from 0.1 to 10.0 on a weight basis.

- 5 9. A method as claimed in claims 5, 7 and 8, wherein the wettable mineral has a particle size of from 0.01 to 0.2 microns and is exploded silicon dioxide, potassium titanate, titanium dioxide, thoria or zirconia.

- 10 10. A method as claimed in any of the preceding claims, wherein the fluorocarbon polymer is in the colloidal state.

11. Porous bodies made by a method as claimed in any of the preceding claims.

- 15 12. A hydrophobic polymeric matrix having preselected wettable characteristics comprising a continuous phase of sintered fluorocarbon polymeric material having a series of integral interconnecting pores and a discontinuous colloidal mineral phase deposited in said pores, said mineral phase being uniformly  
20 arranged from major surface to major surface of said matrix.

- 25 13. A matrix as claimed in claim 12, wherein the particulate fluorocarbon polymer has an average particle size of from 0.1 to 50 microns and the pores have an average diameter of from 0.5 to 10 microns and said

colloidal mineral filler has an average particle size from 0.01 to 0.2 microns.

- 30 14. A matrix as claimed in claim 13, wherein the ratio of fluorocarbon polymer to colloidal mineral filler is from 0.1 to 10.0 on a weight basis.

- 35 15. A matrix as claimed in any one of claims 12 to 14, disposed as an element in an electrochemical cell comprising an anode, a cathode, and an electrolyte, said electrolyte separating said anode and cathode.

16. A matrix as claimed in claim 15, wherein the element is an electrolyte matrix.

- 40 17. A method of preparing a matrix substantially as set forth in the foregoing Example.

- 45 18. A method of preparing a matrix as claimed in claim 1, substantially as hereinbefore described.

19. A matrix prepared by the method as claimed in claim 17 or claim 18.

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